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(72) Inventors DONALD JOHN BARCLAY and
JAMES MICHAEL LINFORD VIGAR

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(54) ELECTROPLATING OF CHROMIUM

(71) We, INTERNATIONAL BUSINESS MACHINES CORPORATION, a Corporation organized and existing under the laws of the State of New York, in the United States of America, of Armonk, New York 10504, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the electroplating of chromium, and more particularly to an electroplating bath for depositing chromium having an anolyte separated from the catholyte by a cation exchange membrane.

The use of membranes in electroplating baths has been suggested but has been inhibited by the fact that formerly they have exhibited high electrical resistance and consequently produced unacceptably high plating voltages in electroplating baths. Also the use of membranes required expensive structural modification of existing electroplating baths.

The present invention provides an electroplating bath for depositing chromium having an anolyte separated from a catholyte by a perfluorinated cation exchange membrane, in which the anolyte includes sulphate ions, and in which the catholyte includes chromium (III) sulphate as the source of chromium and anions for reducing the plating voltage; and said bath having an anode immersed in the anolyte, the material of the anode and the anolyte being determined by their chemical reaction.

The bath of the present invention prevents adverse anode reactions with negligible increase in the plating voltage. One such adverse reaction is the oxidation of Cr(III) ions to Cr(VI), since the accumulation of Cr(VI) ions in a trivalent chromium plating solution ultimately results in the cessation of plating.

The anolyte preferably has a depolarising species therein capable of reducing the electrode potential of the anode when the bath is in use. In addition the pH of the catholyte can be stabilised by arranging the pH of the anolyte to allow hydrogen transport through the membrane to compensate for hydrogen evolution at the cathode.

A preferred perfluorinated cation exchange membrane is a sheet of NAFION. (NAFION is the trade mark of the Du Pont Corporation.) These perfluorinated polymer membranes are thin, have negligible electrical resistance and are mechanically and chemically robust. The depolarising species may include ferrocyanide anions, hydrazine or quinhydrone. The effect of the depolarising species is to significantly reduce the plating voltage. The plating voltage can be further reduced by using highly conducting anions in the catholyte which without the use of a membrane could have produced an adverse anode reaction. An example of this is chloride anions. Chloride anions are desirable as they have high specific conductivity and are obtained from the inexpensive NaCl salt. Their use without a cation exchange membrane is undesirable as chlorine can be evolved at the anode.

The electroplating baths of the present invention, therefore, can avoid deleterious anode reactions, and can reduce the plating voltage by using a perfluorinated cation exchange membrane and by using a suitable anolyte. In this way it is possible to separately optimise both the anolyte and catholyte. In addition the material of the anode is not determined by the plating solution and can be optimised for cost and for its electrochemical reaction with the anolyte.

The anolyte can be contained within an anode arrangement which comprises a compartment having at least a part of its surface formed by a perfluorinated cation exchange membrane, and having within the compartment an anode. The anolyte preferably has a depolarising species therein capable of reducing the electrode potential of the anode when the bath is in use.

The anode arrangement is such that it can be substantially the same shape and size as a conventional anode and can be immersed and supported in the catholyte without changing the anode supports.

One anode arrangement comprises a compartment consisting of a perfluorinated cation exchange membrane supported on a metal or plastic box-like frame and has an anode supported within the compartment. Alternatively the membrane may be in the form of a tube. An anolyte is provided in the compartment or tube, surrounding the anode, preferably by a gel, such as an Agar gel, saturated with a depolarising species. In addition the gel may contain a colloidal dispersion of a metal or carbon to increase the conductivity of the anolyte. The membrane is preferablyna NAFION sheet. This anode arrangement provides a rugged, simple and efficient anode which prevents adverse reactions and enables the catholyte to be optimised for plating. Also the acidity of the anolyte can be arranged so that the pH of the catholyte is stabilised when the bath is in use.

The invention will now be described with reference to the following examples:

EXAMPLE 1

An electroplating bath for chromium comprises an anolyte and a catholyte have the following constituents.

Anolyte

Potassium Ferrocyanide ($K_4Fe(CN)_6$)	1M
Sodium Sulphate (Na_2SO_4)	2M
pH adjusted to	1.6

Catholyte

Chromium (III) Sulphate	0.1M
Sodium thiocyanate	0.2M
Sodium Chloride	2M
Glycine	10 grams/litre
Boric acid	60 grams/litre
Wetting agent (FC98)*	0.1 gram/litre
pH adjusted to	3.5

* FC98 is a product of the 3M Corporation.

The anolyte and catholyte were separated by a sheet of NAFION (NAFION is a trade mark of the Du Pont Corporation). The bath was operated at a temperature of 50°C. The effect of using ferrocyanide as a depolariser in the anolyte was to reduce the plating voltage by 17 percent using a platinised titanium anode. The ferrocyanide anions are oxidised to ferricyanide anions during plating so that the ferricyanide anions must be reduced back to ferrocyanide ions after a given plating time. The depolarising species may be reduced electrochemically in a suitable electrolyte or may be reduced by adding a suitable reducing agent, such as sodium dithionite or zinc, to the anolyte.

In addition the pH of the catholyte may be stabilised by adjusting the pH of the anolyte to allow hydrogen ion transport through the membrane to compensate for the increase in the pH of the catholyte by the evolution of hydrogen at the cathode.

Hydrazine and quinhydrone may be substituted for ferrocyanide anions in the anolyte.

EXAMPLE 2

An anode arrangement for a chromium (III) electroplating bath having a composition similar to the catholyte given in Example 1 consists of a compartment of box-like shape. The compartment consisting of a NAFION membrane supported by a metal or plastics frame. Alternatively the membrane may be in the form of a tube. A carbon anode is supported within the compartment or tube. An anolyte fills the inside of the compartment or tube surrounding the carbon anode. The anolyte consists of an Agar gel saturated with a solution of 2M potassium iodide in 0.1M sulphuric acid. The conductivity of the anolyte can be further increased by including a colloidal dispersion of carbon in the gel. The sulphuric acid concentration can be arranged so that the pH of the catholyte is stablised when the bath is used.

The depolarisation reaction comprises the oxidation of I^- ions to I_3^-. This reaction is reversible allowing the depolarising species to be regenerated (reduced) in an aqueous electrolyte or in the electroplating bath itself by making the anode arrangement a temporary cathode.

Alternatively depolarising species to the iodide anions include ferrocyanide anions, hydrazine, quinhydrone or ferrous ions. Materials other than carbon may be used for the anode. Suitable materials are stainless steel, platinised titanium, magnetite or chromium depending on the specific depolarising species.

EXAMPLE 3

An electroplating bath for chromium comprises an anolyte and a catholyte having the following constituents:

Anolyte

10% by volume sulphuric acid (approximately 2M) and quinhydrone (to saturation at 18°C)

pH adjusted to	1.0

Catholyte

Chromium Sulphate	0.1M
Sodium thiocyanate	0.2M
Sodium chloride	2M
Glycine	10 grams/litre
Boric acid	60 grams/litre
Wetting agent (FC98)	0.1 gram/litre
pH adjusted to	3.5

The anolyte and catholyte were separated by a sheet of NAFION membrane. The bath was operated at a temperature of 50°C. The

use of quinhydrone reduced plating voltage by 15% using a platinised titanium anode mesh.

WHAT WE CLAIM IS:—

1. An electroplating bath for depositing chromium having an anolyte separated from a catholyte by a perfluorinated cation exchange membrane, in which the anolyte includes sulphate ions, and in which the catholyte includes chromium (III) sulphate as the source of chromium and anions for reducing the plating voltage; and said bath having an anode immersed in the anolyte, the material of the anode and the anolyte being determined by their chemical reaction.

2. A bath as claimed in claim 1, in which the anolyte has a depolarising species therein capable of reducing the electrode potential of the anode when the bath is in use.

3. A bath as claimed in claim 2, in which the depolarising species are ferrocyanide anions, hydrazine, quinhydrone, potassium iodide ions in sulphuric acid solution or ferrous ions.

4. A bath as claimed in any one of the preceding claims, in which the pH of the anolyte is arranged to allow hydrogen ion transport through the membrane to compensate for hydrogen evolution at the cathode thereby stabilising the pH of the catholyte.

5. A bath as claimed in any one of the preceding claims, in which the anolyte is contained within a compartment immersed in the catholyte, the compartment having at least a part of its surface provided by the membrane.

6. A bath as claimed in claim 5, in which the anolyte is a gel.

7. A bath as claimed in claim 6, in which the gel has a colloidal dispersion of a metal or carbon therein.

8. A bath as claimed in any one of claims 5, 6 or 7, in which the compartment comprises a metal or plastic box-like frame, or in which the compartment is in the form of a tube.

9. A bath as claimed in any one of the preceding claims, in which the anode is of carbon, platinised titanium, stainless steel, magnetite or chromium.

10. An electroplating bath for depositing chromium substantially as described with reference to Examples 1, 2 or 3.

ALLAN E. MITCHELL,
Chartered Patent Agent,
Agent for the Applicants.

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